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(54) Title: **CROSS-LINKED CATIONIC STARCHES AND THEIR USE IN PAPERMAKING**

## (57) Abstract

A method of making paper comprising the step of adding to a paper furnish, at or prior to the headbox of a paper making machine, a modified starch prepared by swelling a cationised cross-linked starch under conditions selected so that the viscosity of the swollen product is less than 400 cps (measured at 3.0 % w/w starch solids; Brookfield RTV Model viscometer at 70 °C, 100 rpm, No 2 spindle or equivalent). A method of manufacture of a suitably modified starch is also described and claimed.

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**TITLE: CROSS-LINKED CATIONIC STARCHES AND THEIR USE IN PAPERMAKING****FIELD OF THE INVENTION:**

This invention relates to a modified starch and to a method of strengthening paper.

**5 BACKGROUND:**

In the past it has been usual to pass paper from the primary driers of a paper machine to a size press wherein a starch solution is applied to one or both sides of the paper. This coated paper then runs over further driers to reduce the moisture to specification. The amount of starch/water pick up is an important limitation on paper  
10 production speed, particularly on paper grades exceeding 120 GSM (grams per m<sup>2</sup>). The size press unit comprises two rubber coated rolls applying a film of size press starch as the paper web passes through the nip.

In order to improve production speed, to promote microfloculation and enhance strength, some starch has already been added at the wet end of the paper  
15 machine. For this purpose, it is known to use cationic or amphoteric starch or to use starch of large natural grain size or starch swollen with controlled heating with or without alkali.

At present a cationic starch with increased granule diameter can be prepared by diluting a cationic maize starch to about 3.0% (w/w) and heating the slurry in a batch  
20 or jet cooker to a temperature which is carefully controlled to be just below the gelatinisation point of the starch. When the viscosity reaches a preset, desired level, cooling water has to be added immediately to stop further swelling or bursting of the starch granules. A similar swelling method has been used to prepare corrugating starch adhesive. If the temperature is allowed to exceed this swelling temperature for  
25 any length of time, the starch becomes soluble and can subsequently be lost from the fibres with the white water effluent. The application of starch in this manner is limited to 1.5-2.0% maximum.

An alternative method of producing modified starches for paper making has been disclosed in US 5,122,231 wherein a cationic starch is cross-linked to a viscosity  
30 in the range of from 500 cps to about 3,000 cps at a starch concentration of 1.4% (w/w) and at 95°C. (Brookfield viscometer, 20 RPM, No 2 spindle). This cationised,

cross-linked starch is then added to anionic paper pulp during paper manufacture, utilising a neutral or alkaline furnish. It is not clearly described in US 5,122,231 in which form the modified starch is added to the paper stock (ie. gelled or ungelled). The text suggests that the starch performs its function in a cooked or gelled state  
5 where the increased molecular weight (hydrodynamic volume) of the starch polymer due to cross-linking enhances the dewatering ability of the starch and therefore increases the drainage rate of the pulp. At no point does the patent disclose that the modified starch is to be added in a "swollen granule" form.

These abovementioned methods have not produced modified starches that fully  
10 satisfy the requirements of paper making and have not met with commercial success.

It is an object of the present invention to provide a new, modified starch which can be used to improve the process of making and strengthening paper.

#### DISCLOSURE OF THE INVENTION:

According to one aspect the invention consists in a method of making paper  
15 comprising the step of adding to a paper furnish, at or prior to the headbox of a paper making machine, a modified starch prepared by a process comprising the step of swelling a cationised cross-linked starch under conditions selected so that the viscosity of the swollen product has a viscosity of less than 400 cps (as herein defined). Preferably the swollen cationised cross-linked starch has a viscosity of less than 200  
20 cps and more preferably less than 50 cps.

According to a second aspect the invention consists in a modified starch prepared by a process comprising the steps of:

- (a) simultaneously or sequentially cross-linking and cationising starch; and
- (b) swelling the cationised cross-linked starch, the degree of cross-linking  
25 and conditions of swelling being controlled so that the viscosity of the product of step (b) is less than 400 cps (as herein defined).

According to a third aspect the invention consists in a modified starch prepared by a process according to the first aspect comprising the steps of:

- (a) cross-linking starch;
- 30 (b) simultaneously or subsequently cationising the cross-linked starch; and
- (c) swelling the cationised, cross-linked starch, the degree of cross-linking

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and conditions of swelling being selected so that the viscosity of the product of step (b) is less than 400 cps (as herein defined).

In preferred embodiments of the invention starch is cross-linked and simultaneously or subsequently cationised, and more preferably is first cross-linked  
5 and subsequently cationised.

Throughout the specification, references to the viscosity of swollen modified starch are to viscosity in cps as measured at 3.0% w/w starch solids on a Brookfield RTV model viscometer at 70°C, at 100 rpm, using a Number 2 spindle (or as measured by equivalent means).

10 Cross-linking the starch has been found to be an excellent method of controlling the swelling of the granules. The temperature range required to initiate swelling is less demanding and where a range of granule sizes is present in the starch a more uniform swelling occurs.

Cross-linking as described above also enables the starch granules to resist or  
15 substantially withstand the shear forces that occur during the jet cooking and pumping processes during starch preparation and also to withstand those forces encountered within the wet end operations of the paper machine.

It is highly preferred that the degree of cross-linking and conditions of swelling are selected so that the viscosity of the modified starch is less than 100 cps, and more  
20 preferably less than 50 cps. (3.0% w/w solids or RTV Brookfield, 70°C at 100 RPM using No 2 spindle). The swelling is conducted at a selected temperature which is above the gel point of the unmodified starch and desirably, for example, at about 75°C. This swelling temperature will vary according to both the degree of cross-linking and the type of native or unmodified starch used.

25 Cross-linking agents can include STMP (sodium trimetaphosphate), sodium hexametaphosphate, phosphorous oxychloride, phosphate or other polyphosphate compounds, epichlorohydrin, ketone-aldehyde resin, formaldehyde or derivatives thereof. In addition, inhibitors of starch which are capable of raising the gelatinisation point above its natural unmodified gel point may be used. Such inhibitors include  
30 osmotic inhibitors preferably salts.

The amount of cross-linking agent can be 0.05% or more by weight of starch

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solids, most preferably 0.05% to 1.0%.

Starch which can be cross-linked includes all types of native starches, premodified starches or hybrids thereof. Preferably the native starches include eg. potato, maize, tapioca, wheat, rice, waxy maize and high amylose maize. Premodified  
5 starches may be chemically modified for example by treatment with acids, alkalis, enzymes or oxidising agents. Other hybrids including eg. high amylopectin or high amylose starches may also be used. High amylose (75%) has a natural gel point above 100°C and would require modification (eg. hydroxypropylation) to lower its gel point before treatment.

10 Cationisation, may be undertaken either subsequent to or simultaneously with cross-linking. Processes of cationising starch are well known in the art and any suitable process may be used.

Cationisation chemicals include quaternary amine derivatives, dicyandiamine, cyanamide or polyaminoamide epichlorohydrin complexes. Other agents which may  
15 be used are blends of commonly used cationic retention aids such as polyacrylamides and derivatives thereof.

Preferably, the starch is cationised to a degree of substitution (DS) of greater than 0.005, but not greater than 0.05, preferably to a DS of from about 0.01 to about 0.04. The degree of substitution (DS) is defined as the average number of hydroxyl  
20 groups on each anhydroglucose unit which are derivatised with subsequent groups.

Polyaminoamide epichlorohydrin complexes can advantageously be used as this results in simultaneous cross-linking and cationisation of the starch under suitable conditions.

According to a fourth aspect, the invention consists in a method of making  
25 paper comprising the step of adding to a paper furnish at, or prior to, the headbox, an effective amount of modified starch according to the first, second or third aspect. The paper produced according to this method has increased strength.

According to a fifth aspect, the invention consists in a paper made or strengthened in accordance with the invention.

30 An embodiment of the invention, will now be described by way of example only, with reference to the following Figures and Tables:

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## BRIEF DESCRIPTION OF THE DRAWINGS:

Figure 1 shows the distribution of particle size of native potato starch with the x-axis being particle size in  $\mu\text{m}$  and the y-axis being the percentage of particles in the range;

5        Figure 2 shows the distribution of particle size of the potato starch of Figure 1 after being modified according to the process of the invention;

Figure 3 shows the distribution of particle size of native wheat starch; and

Figure 4 shows the distribution of particle size of native wheat starch of Figure 3 after being modified according to the process of the invention.

## 10    BEST MODE OF CARRYING OUT INVENTION:

By way of example of an embodiment of the invention, an aqueous slurry containing 30% (w/w) native starch would be adjusted to pH 10.5 using NaOH and heated to a temperature of  $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . It would then be reacted with 0.1% by weight of starch solids of sodium trimetaphosphate ("STMP"), for several hours to achieve  
15    cross-linking.

At the completion of reaction, the pH would be lowered to 6.0 with HCl and the mixture washed three times with water. The cross-linked product would be cationised using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride at pH 11.0.

The cross-linked, cationic product would be diluted to 3.0% and heated to  
20     $70^{\circ}\text{C}$  via controlled jet cooking to swell the granules. An effective amount of the modified starch, preferably between 1.0% and 10.0% based on the weight of dry fibre in the paper furnish, would then be added to paper pulp at the wet-end stage, just prior to the headbox. As the temperatures at the drying stage of the process would approach  $100^{\circ}\text{C}$ , more particularly about  $95^{\circ}\text{C}$ , the granules would gelatinise within the paper  
25    during drying.

The properties of the modified starch prepared according to the above process were compared with unmodified native starch.

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TABLE 1

Comparison of Properties between native starch and a modified starch according to the invention.			
5    10	a)	Water gain per g starch (g/g)	
		<b>STARCH</b>	<b>NATIVE</b>
			<b>MODIFIED</b>
		Potato	24*
		Wheat	13*
15    20	b)	Gel point range (°C)	
		<b>STARCH</b>	<b>NATIVE</b>
			<b>MODIFIED</b>
		Potato	55-60
		Wheat	60-65
25	c)	Viscosity value at 3.0% starch solids at 70°C (cps) (Brookfield Spindle 2, 100 RPM)	
		<b>STARCH</b>	<b>NATIVE</b>
			<b>MODIFIED</b>
		Potato	200
		Wheat	150
		Tapioca	150

As shown in Table 1 the gel point range of the modified starch is higher than that of the unmodified starch. Such a characteristic is desirable because it enables the degree to which swelling occurs, *to be controlled so that overswelling or bursting does not occur* during cooking. Thus the modified starch will not completely gelatinise until it is applied to the paper furnish and subsequently heated over driers.

In addition it is shown that the maximum degree of swelling of the starch varies with the type of starch used. Preferably a modified starch which has a



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gelatinisation point of up to about 100°C is selected.

Finished paper products were prepared in a laboratory paper making machine and were subjected to burst strength tests and compared with paper to which no starch had been added or to which non-cross-linked starch was added at the same rate. The non-cross-linked starch had been pre-treated by heating a 3.0% w/w slurry at 70°C for 10 minutes.

TABLE 2

Comparison of paper burst strength and particle size			
10	a)	Burst strength test	
		<b>PAPER</b>	<b>BURST STRENGTH (kPa)</b>
		Blank	200
		2.5% standard starch	254
15		2.5% standard, cationic starch	290
		2.5% cross-linked, cationic starch	318
20	b)	Particle size* (micron)	
		<b>STARCH</b>	<b>NATIVE</b>
		Wheat	21.1
		Potato	39.9
			<b>MODIFIED**</b>
			35.0
			99.8
25		* Average diameter	
		Accepted range for wheat native starch	: 2-35 micron
		Accepted range for potato native starch	: 15-100 micron
30		** Starches modified in accordance with the process of the invention	

The results in Table 2 illustrate that modified starch prepared according to the invention has an improved capacity to strengthen paper.

That is, tests on paper strengthened with starches modified according to the invention show that the invention produces a number of desirable qualities. The ability to control the swelling of starch granules to certain sizes enables different

grades of paper with good, uniform quality and strength to be produced. In addition, the capability to add high percentages of starch at the wet end of the paper-making process may provide both an economic and a productivity gain because size-press starch is not then necessary for increased paper strength. This enables the paper machine speed to be improved on heavier grades of paper, thus increasing productivity without sacrificing strength.

The best performance is obtained when the swollen starch granules are carefully controlled. The preferred range is such that 75% of the swollen starch particles are within the range of from 15 to 90 microns. If there are too many small granules (ie. <15 microns) they are susceptible to passing through the paper fibres only to be lost to the backwater. Granules greater than 90 microns tend to be too sparsely spread throughout the paper sheet to provide a uniform strength (ie. less bond points per cubic centimetre of paper). Granule size is controlled primarily by selection of starch or starch blend and by degree of cross-linking.

#### EXAMPLE A

Various starches and blends of starches were prepared and swollen in accordance with the process of the present invention. Each starch or starch blend was slurried in water to a concentration of 32% w/w and 3% sodium chloride added. 2.5% sodium hydroxide solution was then added until a pH of 10.8 was reached.

This mixture was heated to  $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$  and sodium trimetaphosphate (STMP) was added at equivalent to 0.1% on starch. This was allowed to react for 4 hours at  $40^{\circ}\text{C}$ . Further 2.5% sodium hydroxide solution was added until a pH of 12.5 was obtained. Whilst still under agitation a quaternary ammonium compound (QUAB 188) was added at a rate of 8.5% on starch. After reacting for at least 10 hours at  $40^{\circ}\text{C}$  the pH was reduced to 6-7 with hydrochloric acid. Filtration, repeated washing with water and drying produced the final modified starch or starch blend. These starches were then reslurried in water to 3.0% w/w solids and heated to  $70^{\circ}\text{C} \pm 2^{\circ}\text{C}$  where swelling of the granules occurred. These modified starches were added to recycled pulp at a level of 3.7% DS starch on fibre. Percol 182, a well known retention aid used in paper making, was added to the various diluted pulp preparations at a level of 0.04% on fibre, immediately prior to sheet information on the laboratory

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scale paper machine. A laboratory dynamic paper making machine was used to prepare a number of 150 GSM paper sheets which were then pressed and dried at 100°C.

- After conditioning, the hand sheets were tested for ring crush using standard procedures and the results were corrected to exactly 150 GSM basis weight. The cationicity of the starches was similar (approximately 0.016 DS in each case).

TABLE 3

MODIFIED STARCH TYPE/BLEND	PARTICLE SIZE RANGE. (μ)	PAPER RINGCRUSH (N)	FIBRE RETENTION (%)
Blank	15-90 (Fines)	188	85
Potato	90-265	216	88
Tapioca	30-59	252	91
Wheat	43-90	240	90
1:1 Tapioca/Wheat	30-90	257	90
1:1 Potato/Wheat	30-265	205	90
1:4 Potato/Wheat	40-265	210	89
1:1 Potato/Tapioca	30-265	209	90

**EXAMPLE B**

- 10 A further laboratory trial was performed to test the reproducibility of the method. A different fibre sample being waste based and paper machine sourced was used. A modified starch prepared and swollen according to the process of the invention (as described in Example A) was added at a level of 3.8% on fibre. As described in Example A 150 GSM paper sheets were prepared and dried.

TABLE 4

STARCH TYPE	PARTICLE SIZE RANGE ( $\mu$ )	PAPER RING CRUSH (N)	BURST (KPA)	FIBRE RETENTION (%)
Blank	15-90 (Fines)	156	236	84
Modified Tapioca	30-59	217	385	90
Modified Potato	90-265	198	315	90

The above results show that the paper strength is adversely affected where there is a larger swollen starch particle size spread (ie. potato). The best strength results occurred when the particle size range of the starches more closely matched that of the paper fines.

Preferably the modified starches used to improve paper strength characteristics are selected from the group consisting of a blend of equal parts wheat and tapioca starches; tapioca starch; or wheat starch.

#### EXAMPLE C

A modified starch was prepared thus:

- (i) Wheat starch was slurried in water to give 30.0% w/w solids.
- (ii) Dilute sodium hydroxide solution was added to pH 12.5 with good agitation.
- (iii) Mixture was heated to  $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$ .
- (iv) Quaternary ammonium compound (QUAB 188) was added at a rate of 8.5% on starch.
- (v) Mixture was reacted for 10-12 hours.
- (vi) Hydrochloric acid is added to adjust pH to 11.0.
- (vii) STMP was added at a level of 0.1% DSB starch.
- (viii) Mixture was kept stirred at  $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$  for 4-5 hours.
- (ix) pH was reduced to 7-8 with HCl.
- (x) Starch was filtered, washed and dried.

It was found that the modified starch prepared by this method when swollen at  $70^{\circ}\text{C}$  at 3.0% solids performed in a similar manner to those starches prepared in

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Example A.

### EXPERIMENTAL TRIAL A

11,000 kg of 20.0% solids slurry of the cross-linked cationic starch was prepared (as per Example A). The starch blend used was 10.0% tapioca starch, 85.0%  
5 normal wheat starch and 5.0% fine grain wheat starch. This modified starch blend was transported to a recycled paper mill where it was diluted to 4.0% DSB solids with water and subjected to a temperature of 70°C to swell the starch granules. The swollen starch was then added to the bottom ply machine chest furnish at a rate of 60.0% of total and at 40.0% of total to the top ply machine chest thick stock. The  
10 rates of addition were increased over a 4 hour period to give a final starch to fibre level of approximately 3.5% DSB on dry fibre for the 150 GSM Paper.

At the near completion of a jumbo roll of paper, the size press starch application was temporarily replaced with water sprays to provide paper samples containing only the wet end modified starch. Other running parameters were recorded  
15 during the trial duration.

At the time of the trial the paper machine was using a bentonite - acrylamide retention system which is normal practice in this particular mill. No alteration was made to the addition rates of these chemicals during the trial.

The following results were obtained:

- 20 1. Drainage on wire and the wet line were unaffected by the addition of the modified starch blend.
2. First pass retention increased from 85.0% to 88.0% during the duration of the trial.
3. White water solids decreased from 1200 ppm to 900 ppm during the trial.
- 25 4. Ring crush results of up to 243N were obtained with only the modified wet end starch in the paper (ie. no size press starch addition). This compares favourably to a range of 240 - 260N for 4.0% size press starch addition (starch on fibre).
5. The actual starch percentage in the paper sheet ranged between 3.0% and 3.3% which was limited by the delivery pump capacity.

30 This plant trial proved that commercially acceptable paper could be produced from 100% recycled furnish without the use of the size press.

Based upon the teaching herein, the invention may be embodied in other forms and may extend to other applications which would be within the knowledge and expertise of those skilled in the art. In particular it has been found that the above described invention can be also used with micro particulate retention systems (such as colloidal silica or bentonite systems).

#### EXPERIMENTAL TRIAL B

8,000 kg of 37.0% solids slurry of cross-linked cationic starch was prepared (as per Example A). The starch used was 100% wheat starch with a normal bimodal distribution of particle size. This modified starch was delivered to a recycled paper mill where it was diluted to 6.0% solids with water and cooked via a jet cooker to 70°C to swell the starch granules.

This swollen modified starch was then dosed at 1,750 litres/hour to the top ply machine chest and 3,500 litres/hour to the bottom ply machine chest. The two ply paper was a 150 GSM basis weight paper for corrugating medium. The dosage rate equated to 3.07% starch on fibre.

During the trial some paper was produced without any size press starch which had been previously added at a rate of 5.49% on fibre, thus providing a paper sample containing only the modified swollen wet end starch.

The following results were observed:

1. Machine speed was not unduly affected by the addition of the wet end modified starch.
2. First pass retention increased from 76.0% to 82.0% during the trial.
3. The actual starch percentage in the paper sheet ranged between 2.9% and 3.1% on fibre and was limited by the delivery pump capacity.
4. The CMT (Concora) increase was 33 Newtons per 1.0% of wet end starch addition versus only 25 Newtons per 1.0% of size press starch.

Again this plant trial proved that commercially acceptable paper could be produced from 100% recycled furnish without the need for size press addition.

## CLAIMS:

1. A modified starch prepared by a process comprising the steps of:
  - (a) simultaneously or sequentially cross-linking and cationising a starch; and
  - (b) swelling the cationised cross-linked starch, the degree of cross-linking
- 5 and conditions of swelling being selected so that the viscosity of the product of step (b) is less than 400 cps (as herein defined).
2. A modified starch according to claim 1 wherein the process comprises the steps of:
  - (a) cross-linking the starch;
  - 10 (b) simultaneously or subsequently cationising the cross-linked starch; and
  - (c) swelling the cationised cross-linked starch, the degree of cross-linking and conditions of swelling being selected so that the viscosity of the product of step (c) is less than 400 cps (as herein defined).
3. A modified starch according to claim 1 or claim 2, wherein the starch is first
- 15 cross-linked and subsequently cationised.
4. A modified starch according to any one of the preceding claims, wherein the viscosity of the product is less than 100 cps.
5. A modified starch according to any one of the preceding claims, wherein the viscosity of the product is less than 50 cps.
- 20 6. A modified starch according to any one of the preceding claims, wherein the swelling is conducted at a selected temperature being above the temperature at which the unmodified starch is gelatinised.
7. A modified starch product according to claim 6, wherein the selected temperature is below 90°C.
- 25 8. A modified starch product according to any one of the preceding claims, wherein the cationised cross-linked starch is swollen to a particle size such that 75.0% of the particles are within the range of from 15 to 90 microns.
9. A modified starch according to any one of the preceding claims, wherein the starch is cross-linked by means of a cross-linking agent selected from the group
- 30 consisting of epichlorohydrin; phosphate; polyphosphate compounds; phosphorous oxychloride; ketone-aldehyde; formaldehyde or derivatives thereof.

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10. A modified starch according to claim 9, wherein the cross-linking agent is sodium trimetaphosphate or sodium hexametaphosphate.
11. A modified starch according to claim 10, wherein the cross-linking agent is sodium trimetaphosphate.
- 5 12. A modified starch according to any one of the preceding claims, wherein cationising is conducted by means of a cationisation agent selected from the group including quaternary amine derivatives; dicyandiamine; cyanamide and polyaminoamide epichlorohydrin complexes.
13. A modified starch according to claim 1 or claim 2, wherein polyaminoamide  
10 epichlorohydrin complexes simultaneously cross-link and cationise the starch molecules.
14. A modified starch according to any one of the preceding claims, wherein the cross-linked starch is cationised to a degree of substitution of between 0.005 and 0.05.
15. A modified starch according to any one of the preceding claims, wherein the starch molecules are derived from native starches, premodified starches or hybrids  
15 thereof.
16. A modified starch according to claim 15, wherein the native starches are selected from the group including potato, maize, tapioca, wheat, rice, waxy maize and high amylose maize.
17. A modified starch according to claim 15, wherein the starches are premodified by  
20 chemical means, mechanical means or both mechanical and chemical means.
18. A modified starch according to claim 17, wherein the starches are chemically modified by treatment with acids, alkalis, enzymes or oxidising agents.
19. A modified starch according to claim 17, wherein the starches are mechanically modified by shearing.
- 25 20. A method of making paper comprising the step of adding to a paper furnish, at or prior to the headbox of a paper making machine, a modified starch prepared by a process comprising the step of swelling a cationised cross-linked starch under conditions selected so that the viscosity of the swollen product has a viscosity of less than 400 cps (as herein defined). Preferably the swollen cationised cross-linked starch has a viscosity  
30 of less than 200 cps and more preferably less than 50 cps.
21. A method of making paper comprising the step of adding to a paper furnish, at or



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prior to the headbox of a paper making machine, an effective amount of modified starch according to any one of the preceding claims.

22. A method of making paper according to claim 1, wherein the modified starch is retained within the paper sheet by means of its charge and physical dimensions.

5 23. A method of making paper according to any one of claims 21 or 22, wherein the modified starch fully gelatinises within the paper sheet during the drying step of the paper.

24. A method of making paper according to any one of claims 21 to 23, wherein the modified starch is added at a rate of between 1.5% and 10.0% based on the weight of dry  
10 fibre in the paper furnish.

25. Paper product made according to the method of any one of claims 21 to 24.

26. A process comprising the steps of:

- (a) simultaneously or sequentially cross-linking and cationising starch; and
- (b) swelling the cationised cross-linked starch, the degree of cross-linking  
15 and conditions of swelling being controlled so that the viscosity of the product of step (b) is less than 400 cps (as herein defined).

27. A process according to claim 26 comprising:

- (a) cross-linking starch;
- (b) simultaneously or subsequently cationising the cross-linked starch; and
- 20 (c) swelling the cationised cross-linked starch, the degree of cross-linking and conditions of swelling being controlled so that the viscosity of the product of step (c) is less than 400 cps (as herein defined).

28. A process according to claim 26 or 27 comprising:

- (a) cross-linking the starch; and
- 25 (b) subsequently cationising the cross-linked starch.

29. A process according to any one of claims 26-28, wherein the conditions of swelling are controlled so that the viscosity is less than 100 cps.

30. A process according to claim 29, wherein the conditions of swelling are controlled so that the viscosity is less than 50 cps.

30 31. A process according to any one of claims 26 to 30, wherein the swelling is conducted at a selected temperature being above the temperature at which the

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unmodified starch is gelatinised.

32. A process according to claim 31, wherein the selected temperature is below 90°C.

33. A process according to any one of claims 26 to 32, wherein the cationised cross-linked starch is swollen in step (c) to a particle size such that 75.0% of the particles are within the range of from 15 to 90 microns.

34. A process according to any one of claims 26 to 33, wherein the starch is cross-linked by means of a cross-linking agent selected from the group consisting of epichlorohydrin; phosphate; polyphosphate compounds; phosphate oxychloride; ketone-aldehyde; formaldehyde or derivatives thereof.

35. A process according to claim 34, wherein the cross-linking agent is sodium trimetaphosphate or sodium hexametaphosphate.

36. A process according to claim 35, wherein the polyphosphate compound is sodium trimetaphosphate.

37. A process according to any one of claims 26 to 36, wherein the cationising is conducted by means of a cationisation agent selected from the group including quaternary amine derivatives; dicyandiamine; cyanamide and polyaminoamide epichlorohydrin complexes.

38. A process according to claim 26 or 27, wherein polyaminoamide epichlorohydrin complexes simultaneously cross-link and cationise the starch molecules.

39. A process according to any one of claims 26 to 38, wherein the cross-linked starch is cationised to a degree of substitution of between 0.005 and 0.05.

40. A process according to any one of claims 26 to 39, wherein the starch molecules are derived from native starches, premodified starches or hybrids thereof.

41. A process according to claim 40, wherein the native starches are selected from the group including potato, maize, tapioca, wheat, rice, waxy maize and high amylose maize.

42. A process according to claim 40, wherein the starches are premodified by chemical means, mechanical means or both mechanical and chemical means.

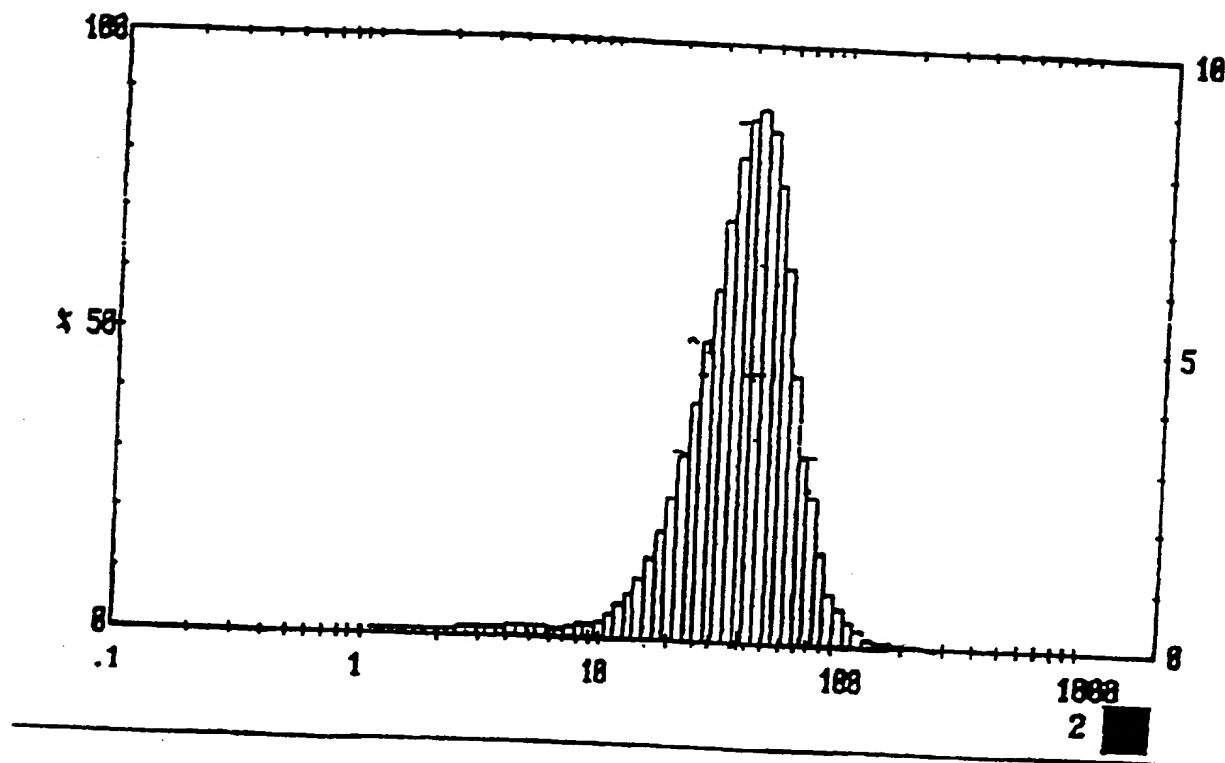
43. A process according to claim 42, wherein the starches are chemically modified by treatment with acids, alkalis, enzymes or oxidising agents.

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44. A process according to claim 42, wherein the starches are mechanically modified by shearing.
45. A modified starch prepared according to any one of claims 1 to 20, substantially as herein described with reference to any one of the Examples and/or accompanying  
5 Figures.
46. A method of making paper according to any one of claims 21 to 25 which method is substantially as herein described with reference to any one of the Examples and accompanying Figures.

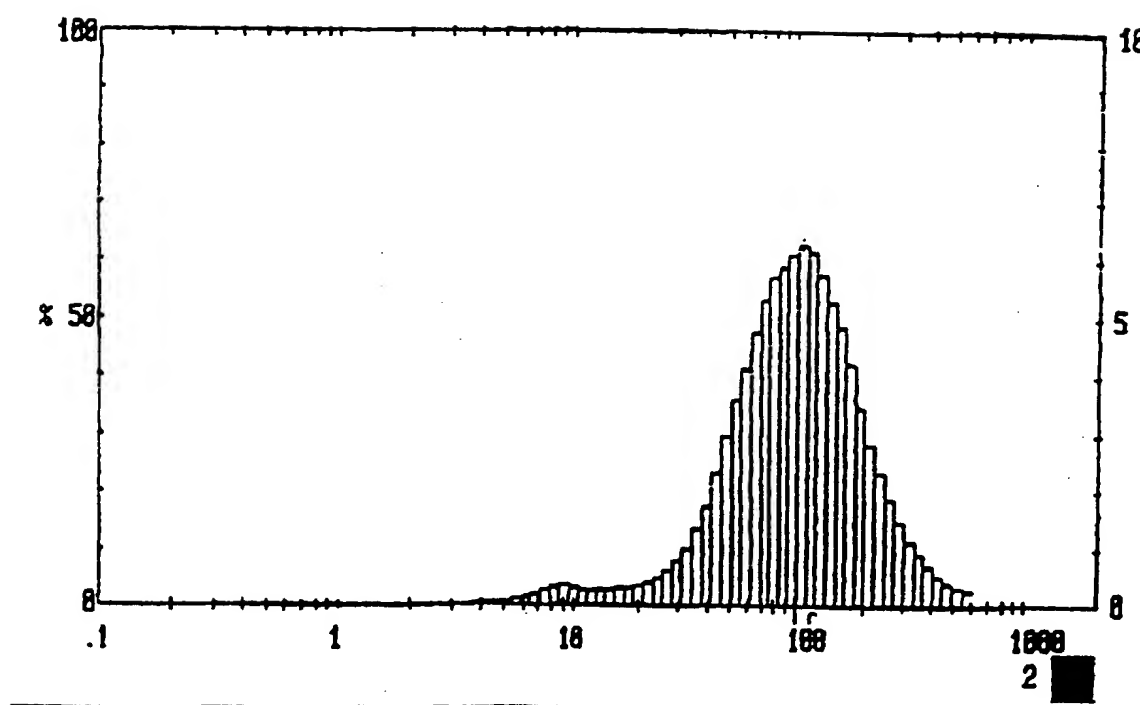
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FIGURE 1



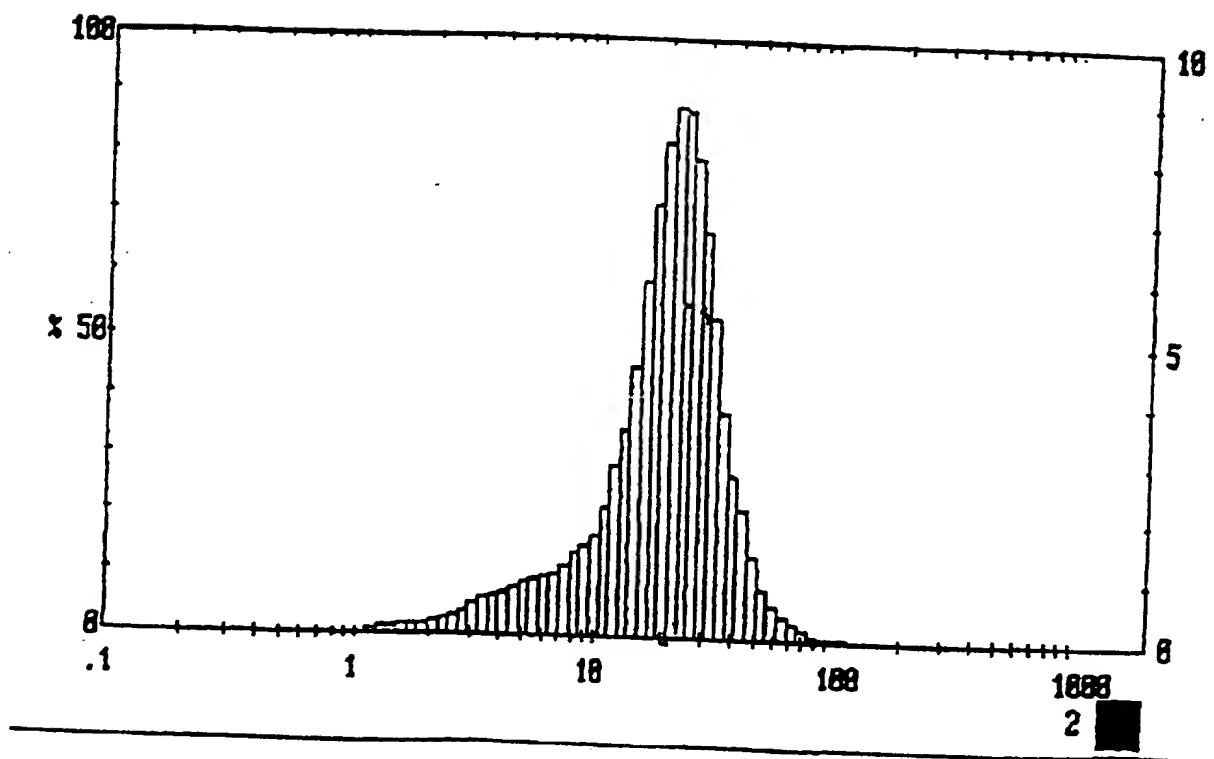
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FIGURE 2



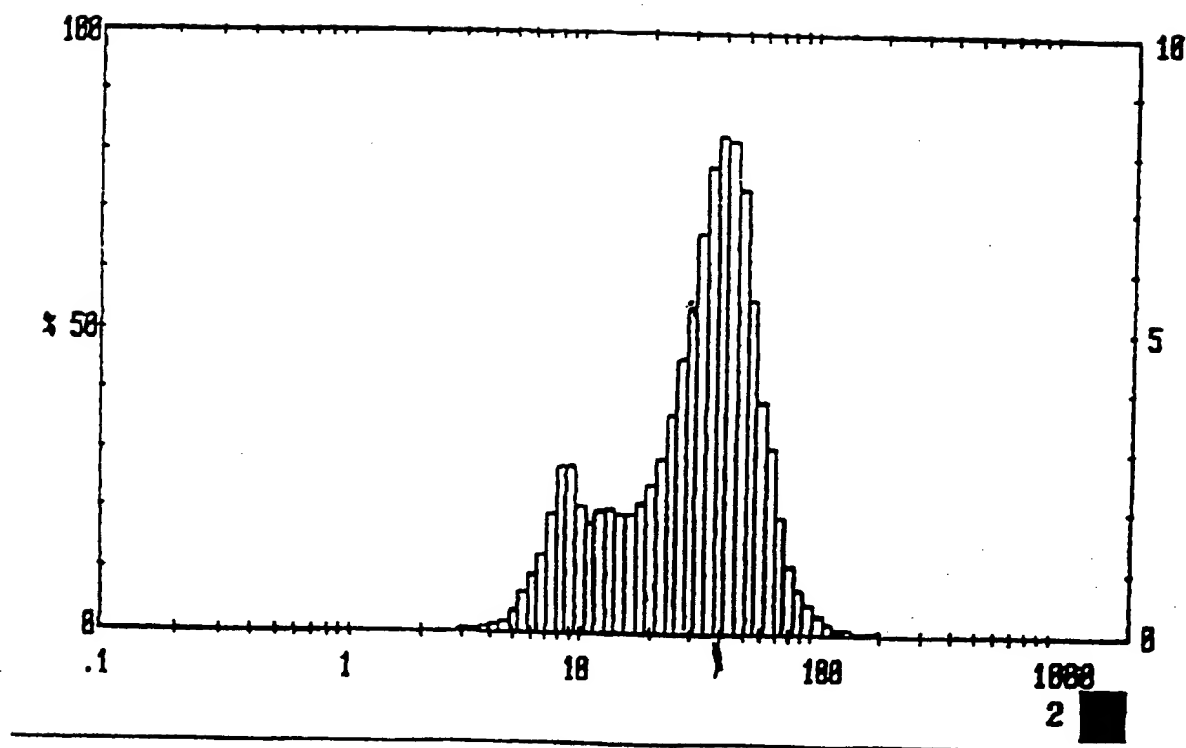
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FIGURE 3



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FIGURE 4



## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/AU 97/00327

**A. CLASSIFICATION OF SUBJECT MATTER**

Int Cl<sup>6</sup>: C08B 31/12 : D21H 17/29, 21/18

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Chemical Abstracts: starch(es) + cationi? + crosslink?

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 603727. A1 (NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION) 29 June 1994 Tables 4 and 7	1-46
D. A	US 5122231. A (ANDERSON) 16 June 1992 Whole document	1-46
A	US 3884909. A (KIGHTLINGER et al) 20 May 1995 Whole document	1-46

☒ Further documents are listed in the continuation of Box C

☒ See patent family annex

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance  
 "E" earlier document but published on or after the international filing date  
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
 "O" document referring to an oral disclosure, use, exhibition or other means  
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
 "&" document member of the same patent family

Date of the actual completion of the international search  
13 June 1997

Date of mailing of the international search report

19 JUN 1997

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C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3778431, A (KIGHTLINGER et al) 11 December 1973 Whole document	1-46

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/AU 97/00327

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims: it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International Application No.

**PCT/AU 97/00327**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	603727	AT	150502	BR	9305197	CA	2112197
		DE	69309018	FI	935804	JP	6212595
		US	5368690	ZA	9309561	US	5523339
US	5122231	NONE					
US	3884909	CA	997337	US	3778431		
US	3778431	CA	997337	US	3884909		
END OF ANNEX							

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